

# Health Effects of Combustion By-Products

by Adel F. Sarofim<sup>1</sup> and William A. Suk<sup>2</sup>

## Introduction

A conference on the Health Effects of Combustion By-Products, co-sponsored by the National Institute of Environmental Health Sciences (NIEHS) and the National Science Foundation (NSF), was held October 23–24, 1990. The objectives of the organizing committee, composed of eight members evenly balanced between those with engineering and health backgrounds, were to provide a review of the sources, fate and transport, and health effects of combustion by-products of importance to incinerator emissions. The membership of the organizing committee and participants of the conference program are in Appendix A. Appendix B contains a reading list for further details of the presentations discussed in this report.

The first session was chaired by W. Suk (NIEHS) and W. Grosshandler (NSF). D. Rall (NIEHS) opened the conference by reviewing the aims of the four NIEHS conferences designed to pinpoint major areas related to toxic chemicals and toxic wastes. The first conference dealt with the fascinating possibilities for the use of biomarkers in epidemiology. Human epidemiology has many problems, including those of identifying populations to study and estimating their exposure. Epidemiology can be made a more precise discipline by using a variety of biomarkers. The second conference dealt with biodegradation and the many avenues available to explore this attractive method of waste remediation. The next conference was on exposure assessment. Biological scientists are criticized for not being able to precisely predict the health effects in a large population. Although exposure measurement is easy in principle, it is difficult to determine the distribution of exposures in a large population. Clearly, there is a need for such assessments when dealing with the many aspects of the potential health effects of combustion by-products, the subject of the last of the four conferences. The topics of the conference are current research on emissions from

incinerators, the mechanisms of formation of combustion by-products, and their impact on human health. Rall also paid tribute to Norton Nelson, who in many ways is the father of the integrated basic research program directed at the health effect problems associated with Superfund sites. This was followed by presentations on the role of incineration in the remediation of Superfund sites.

J. Schofield (Incineration Technology, Inc.) discussed the global trends in incineration technology responsive to concerns related to emissions of organics and metals. These depend strongly on the composition of the waste, incinerator design, and operating conditions and the downstream pollution control equipment. The technology is evolving responsive to increasing environmental regulations, with an attendant significant reduction in emissions and increase in cost. Much of the capital cost of an incinerator is now for pollution control equipment. The trends toward increasing sophistication of the treatment of incinerator effluent streams is expected to continue.

Regulation of emissions are more stringent in Europe than in the United States. The opinion was expressed that incineration in the United States was hurt by weak regulations. J. Hirschhorn (EnviroSearch) stressed that public concerns must be respected. Opposition to incineration is growing, and there is a need to demonstrate that the public health is protected. The tactic of environmental groups has been to attack incineration generically. Public opposition might be softened if different categories of incineration were examined separately. Two of the speakers felt that the biggest need for incineration is for on-site units. For remediation of Superfund sites, the effectiveness of incineration needs to be compared with that of competing technologies.

The wide range of designs available for burning wastes and representative emissions from incinerators were reviewed by R. Seeker (Energy and Environmental Research Corporation). The principal factor governing the design of an incinerator is the physical state of the waste stream. For example, mass-burn municipal solid-waste incinerators use reciprocating grates that are able to handle waste without preprocessing; hazardous waste incinerators often use rotary kilns because of their versatility; and fluidized beds find use in handling finely divided wastes and sludges. Significant volumes of wastes are also burned in industrial furnaces and cement kilns. The largest technical issue in using incinerators is that of assuring high performance while

<sup>1</sup>Massachusetts Institute of Technology, Boston, MA.

<sup>2</sup>Superfund Basic Research Program, Division of Extramural Research and Training, National Institute of Environmental Health Sciences, P.O. Box 12233, Research Triangle Park, NC 27709.

Address reprint requests to Superfund Basic Research Program, Division of Extramural Research and Training, National Institute of Environmental Health Sciences, P.O. Box 12233, Research Triangle Park, NC 27709.

burning a highly variable waste stream. Selected data on emissions were presented. Mean levels of organic emissions of 7 ppm and concentrations of the higher congeners of the dioxins (tetra through octa) of 10 ng/m<sup>3</sup> have been achieved by a combination of better combustion practices and the adoption of more sophisticated air pollution control devices. Metal emissions are the major source of risk associated with incinerators. The metals in the feed will be distributed between the residue, fly ash, and air emissions from an incinerator in proportions that will depend on the metal volatility and on combustion conditions. Increases in combustion temperature and increases in chlorine content of the feed increase metal volatility, and there is a trade-off between increased destruction of organics and increased vaporization of metals in selecting an optimum combustion temperature. The increased understanding of the factors governing emissions have led to improvements in performance, but there remain a number of gaps in the description of emissions.

## Organic Compounds

The second session on organic emissions was chaired by R. Sawyer, (University of California, Berkeley) and D. Patton (EPA, Risk Assessment Forum). The first two talks were on the formation and health effects of benzene and polycyclic aromatic hydrocarbons, which are among the more extensively studied and better understood combustion by-products, both from a standpoint of their formation in flames and their impact on human health.

In his presentation on flame synthesis of benzene and polycyclic aromatic hydrocarbons (PAH), J. Howard (MIT) discussed how mechanistic understanding of the formation of PAH of health concern is pertinent to the identification of technical options for emissions control. Single-ring compounds such as benzene and phenyl radical, representing the first step of PAH formation, are of special interest. Recent research progress includes experimental measurement of free-radical reaction intermediates in flames, theoretical study of elementary reactions hypothesized as critical steps in the initial synthesis and subsequent growth of cyclic structures, and computer analysis and testing of detailed reaction mechanisms consisting of up to several hundred elementary reactions. Reactions of acetylene with the radicals C<sub>4</sub>H<sub>3</sub> and C<sub>4</sub>H<sub>5</sub> and recombination of C<sub>3</sub>H<sub>3</sub> radicals are important in the synthesis of the first ring, whereas the addition of acetylene and recombination of radicals such as C<sub>3</sub>H<sub>3</sub> at radical sites in the PAH structures appear to be important in the formation of additional rings. Recognition of the role of vibrationally excited, highly reactive intermediates, which react before they can be collisionally stabilized, has improved fundamental understanding of the mechanisms. The recent progress constitutes a significant step toward a quantitative basis for emissions control.

Comparable progress has been made in identifying the metabolites of benzene implicated in benzene-induced carcinogenesis. M. Smith (University of California, Berkeley) introduced his talk by noting the enormous economic incentive of determining the risk at low doses of benzene exposures. Extrapolation from the effects on workers subjected to high part-per-million exposures to levels of 0.01–0.001 ppm in air is not possible from epidemiological studies or from standard carcinogenic bioassays. Smith described a series of mechanistic studies aimed at filling this gap by determining the metabolites

or mixture of metabolites responsible for the genotoxic and carcinogenic effects of benzene. From experiments using mice and human cell cultures, he has concluded that the effects of benzene are most likely produced by a mixture of its metabolites. For example, the combination of hydroquinone and catechol is potent in producing numerical chromosome-type aberrations in human cells. He also suggested that the mixture of metabolites responsible for carcinogenicity is probably different from those responsible for myelotoxicity, with phenol and hydroquinone being implicated for the latter. In screening human populations, it will be necessary therefore to look for several metabolites in protein adducts. The other important implication of the findings on mechanism is that, when there are several metabolites involved, the dose-response relationship is likely to be nonlinear.

J. Ross (EPA) discussed the formation and persistence of PAH-DNA adducts, using benzo[*a*]pyrene (BaP) as illustrative of other polycyclic aromatic hydrocarbons. The goal is to measure the delivered dose in the target tissue of the target organ. This is not practical in many cases, and the DNA adducts in peripheral blood lymphocytes can serve as surrogates because of their accessibility. The underlying assumption is that there is a correlation between DNA adducts in the peripheral blood lymphocytes and those in the target tissue. Studies designed to test this hypothesis were conducted on rats for which a correlation was found with peripheral blood lymphocyte adducts and those in the liver and lung. The identities of the adducts produced are also of interest, and for BaP several DNA adducts are produced in each tissue. Studies in rats with BaP and several synthetic metabolites showed significant tissue-specific differences in the types of adducts produced. BaP-diol epoxide-N<sub>2</sub>-deoxyguanosine is the major DNA adduct produced in rat blood, liver, and lung. Ross also reported that an additional major adduct in the liver derived from BaP-7,8-dihydrodiol and an additional adduct in the lung, derived from further metabolism of 9-hydroxy-BaP, may be mechanistically significant in contributing to the tissue specificity of BaP carcinogenicity.

Results of thermal studies of five multicomponent mixtures of potentially toxic materials were reported by B. Dellinger (University of Dayton Research Institute) at temperatures up to 1000 °C, residence times up to 2 sec, and various oxygen levels. These studies suggest that both the pyrolysis and oxidation of mixtures result in a complex mixture of products of incomplete combustion (PICs), many of which may not be produced by any other known process, other than combustion. The pyrolysis of chlorinated or brominated materials can result in potentially significant yields of halogenated polynuclear aromatic compounds, whereas oxidation can result in formation of halogenated dibenzofurans. Thermal degradation of nitrogen-containing materials can result in formation of highly stable and biologically active aliphatic and aromatic nitriles. It is suggested that a more detailed understanding of PIC formation pathways is needed to identify possibly ultra-trace, biologically active species through target GC-MS chemical analysis. Coupling of detailed chemical analysis of thermal reactor effluents with toxicological testing is recommended to identify markers of biological activity for chemically complex samples.

Paradigms for analyzing the health effects of complex mixtures were then presented by W. Thilly (MIT). In real human experience, greater than 10<sup>4</sup> xenobiotic substances are processed

internally by sequential matrices of greater than  $10^2$  metabolizing enzymes and greater than  $10^2$  chromatin repair enzymes. The set of approximately  $2^7$  cell types in the human body presents the probability that each cell type will process a particular chemical in a unique way. The fact that different tissues appear to require a different set of specific mutations to create a cancer cell also must be part of the analysis. Two arguments were presented as the basis for a rational approach to analysis: (a) the specificity of mutational spectra for a particular mutagen in a particular tissue and (b) the log normal approximation of the universal distribution of all chemicals with regard to actual concentration and mutagenic activity in the human body. It was argued that in human experience only one, perhaps two, of the mutagenic stimuli encountered will be responsible for the particular mutations observed in a specific tissue. Rapid progress is being made in developing tools to assay exposure and potential effects.

The discussion centered around the quantification of risks for incinerator emissions. It was noted that risk assessment was complicated by the multiplicity of effluent streams, by the large number of chemicals involved, and by the need to consider multiple disease outcomes. Air emissions often receive most of the attention. Fugitive emissions, leachates from the solid residue, and any scrubber liquids also need to be taken into consideration. The difficulty of completely characterizing the effluent streams and the impracticality of conducting toxicological studies on all compounds was then noted. Current risk assessments, by default, rely heavily on toxicological studies conducted on bacteria or animals. The techniques under development using protein adducts and DNA mutational spectra are very promising as a means of addressing exposure and genetic change in humans but do not provide information on other disease outcomes. Reliance will continue to be placed on the traditional risk assessment paradigm of hazard identification, dose-response assessment, exposure assessment, and risk characterization, although such risk assessments invariably raise many questions about what we do not know. The need for prioritization in filling in the knowledge gaps was evident, a process that would benefit from the interdisciplinary approaches bringing together the talents of the physical scientists capable of characterizing and quantifying exposure with those of the biological scientists with their abilities of determining the compounds of health concern and quantifying their effects.

## Metals

The session on metals was chaired by R. Flagan (California Institute of Technology) and J. Fouts (NIEHS), with initial presentations by J. Wendt (University of Arizona) and A. Fontijn (Rensselaer Polytechnic Institute) on the factors affecting the emission of metals. In combustion research, much of the work on the fate of metals has focused on the observed enrichment with volatile species of the fine aerosol produced by vaporization and condensation in an incinerator. In studies of the health effects of metals from combustion systems, a variety of exposure routes have been identified, with atmospheric emissions being a minor contributor in many cases. The coupling between combustion research and health effects is complex, with indirect routes accounting for much of the health risk. Metal emissions from incinerators must be treated as a multimedia problem. Atmospheric emissions of particulate matter are but one facet. Land

disposal of slag and ash from hoppers at the bottom of the incinerator, collected fly ash from dry particle removal systems such as electrostatic precipitators and fabric filters, and scrubber brine may all contribute to the release of metals to the biosphere. The collection efficiency of particle control devices such as electrostatic precipitators is size dependent, with the submicron particles being most difficult to collect. Fine particles and their associated metals are preferentially emitted, so to the extent that stack emissions are a problem, the submicron particles are most important. Even when efficient particle removal systems are used, particle size may be an important determinant in biological effects. Small particles present large surface areas that may enhance leaching rates when the fly ash is landfilled, for example.

The combustion process does influence the nature of the problem by determining the distribution of potentially hazardous materials with respect to particle size, the oxidation state of the material, and the ease of release to ground or surface waters. High-temperature combustion can increase the production of fine particles by increasing mineral volatilization. Those materials that volatilize concentrate in the fine particles upon condensation. The thermodynamics of metal vaporization are complex and incompletely understood. Direct vaporization of inorganic species has received considerable attention, but metals organically bound in the waste may be released quite readily as well.

Studies of fine particle formation from reactive metal compounds have revealed an additional mechanism of formation of submicron particles. Beginning with aqueous solutions of metal salts, lead and cadmium exhibited the expected temperature dependence of fine particle formation, supporting the hypothesis that vaporization is the major mechanism of fine particle formation. Nickel, on the other hand, would not be expected to vaporize and showed no temperature dependence. Nonetheless, substantial quantities of submicron aerosol were produced, suggesting that explosive fragmentation of the aqueous droplets formed the fine particles. Fragmentation of cenospheres and porous chars may also lead to fine particle formation. The latter mechanisms would introduce nonvolatile species into the fine particles, but would not be expected to lead to enrichment as has been observed with volatile species.

In spite of the importance of the high temperature chemistry of metals, few studies of the associated chemical mechanisms and kinetics have been reported. Those few that appear in the literature are derived from the propulsion literature. From that field it is known that models that assume chemical equilibrium (as current waste incineration models of metallic species do for lack of other input information) can be misleading: reactions can be too slow to achieve equilibrium, faster reactions can interfere, and equilibrium overshoots can readily occur. More realistic models require temperature-dependent kinetic and transport data, coupled with sensitivity analysis. Because the high-temperature chemical reactions determine the oxidation states of the material, they have direct bearing on the environmental hazard of incineration systems. For example, chromium is not particularly toxic as Cr(II), but is extremely toxic as Cr(VI). Studies of the mechanisms of nickel carcinogens reveal that soluble forms of nickel are not carcinogenic, but that crystals of nickel are encapsulated by cells, where they are transformed to the active  $\text{Ni}^{2+}$  form. Factors in the combustion process that influence the form of the metals emitted to the atmosphere or collected and

disposed of on land may, therefore, profoundly influence the health risk of the combustion technology.

The one metal for which atmospheric emissions clearly dominate is mercury. Due to its high vapor pressure, most mercury is released from combustion systems as vapor. Coal combustion is the dominant source. Mercury has a remarkable ability for bioaccumulation, particularly in plankton and fish. It is the only contaminant known to have bioaccumulated to the levels that have an impact on humans. Arsenic and selenium are sufficiently volatile that vapor release may be important as well. For these species, therefore, particle control technologies may not be effective. Alternate control technologies are needed. Capture of metal vapors in an incinerator may be possible. For example, lead may be captured by injection of kaolin injected into the combustion chamber.

An understanding of the thermochemistry of metals in combustion environments may have important benefits even if atmospheric emission of metals is not a critical problem. High temperatures limit hydrocarbon emissions. Because modern systems for removing particles from flue gases are very efficient, the increased fine particle formation with high combustion temperatures may not be a serious drawback. However, if the leachability of the collected ash is enhanced, the ultimate release to the biosphere may also be accelerated. Sorption of metal vapors has been demonstrated as a possible technology that may have benefits beyond the control of stack emissions. With appropriate sorbents, the metals may be captured in a matrix that minimizes leaching.

The session then turned to a discussion of the health effects of four metals often implicated in emissions from incinerators. M. Costa (New York University) addressed nickel carcinogenesis. Nickel is a well-established human carcinogen. It is known that not all nickel compounds have equal carcinogenic potency and that insoluble compounds are most active. A reason for this has been established as the increased bioavailability of compounds such as nickel subsulfide when in the crystalline versus the amorphous state. Studies on the fibroblast cells of the embryo of the Chinese hamster indicated that it is the negative charges on crystals that induces phagocytosis. The phagocytized nickel dissolves and attaches selectively to the heterochromatic region within the genome of the Chinese hamster. From cell-growth studies, a gene on the X chromosome of the Chinese hamster that suppresses senescence has been identified. Many nickel-transformed cells studied so far showed an inactivation of the senescence suppressor gene, which may be an important component of the complex multistep process leading to nickel carcinogenesis.

C. Klaassen (University of Kansas Medical Center) reviewed the role in cadmium toxicity of metallothionein, a cytoplasmic protein with a molecular weight of 6800 that has a high cysteine content and an ability to bind 7 moles of cadmium. The acute hepatotoxicity of cadmium can be prevented by pretreatment with smaller doses of cadmium. Tolerance to acute doses of cadmium is developed by the increased production of metallothionein in the liver as a protection to cadmium injury, a hypothesis supported by the tolerance to acute doses of cadmium of newborn rats, whose liver metallothionein concentration is 25 times that of adults. The metallothionein ties up the cadmium in the liver

as cadmium metallothionein (CdM), thereby reducing but not eliminating liver injury. The CdM is believed to be responsible for the nephrotoxicity of cadmium as a consequence of the transfer in the blood of CdM from the liver to the kidney. Support (but not proof) for this mechanism is provided by the delay in injury of the kidney relative to the liver in chronic exposure tests.

P. Landrigan (Mt. Sinai School of Medicine) introduced his talk by reviewing the major uses of and paths of exposure to lead. The effects of lead poisoning on children and adults are the same although the dose-response is not. Of particular concern are damages to the central and peripheral nervous systems that are permanent and untreatable. Recent studies are on low-dose exposures that are manifested in such ways as subtle deficits in learning disabilities, reduced attention span, diminished vigilance. For example, it has been shown that the IQs of those with a low and high exposure to lead, as determined from tooth lead concentrations, differed by a mean of 7–8 points with more serious differences at the extremes. Correlation of the lead level of newborns with mental development scores shows that the effect of lead is manifested at levels previously considered to be safe. Mental development scores showed a clear gap between those with blood lead levels at birth of  $1.8\mu\text{g/L}$  and  $14\mu\text{g/L}$ , a discernable effect at concentrations below the Center for Disease Control cautionary level of  $25\mu\text{g/L}$ . The role of incinerators in contributing to the exposure is unknown but is probably more through the leachate from the residues and ash than the stack emission. Reduction at the source through recycling and elimination of all but the most essential uses of lead was advocated.

The final presentation in the metal emission session, by T. Clarkson (University of Rochester), dealt with the health effects of mercury. Mercury, emitted primarily as the metal vapor from a variety of sources, has a long atmospheric half-life and is globally distributed. It is deposited mainly as the divalent ion and is methylated by microorganisms to methyl mercury. The major route for human exposure is fish consumption, as the bioconcentration factor for fish high in the trophic chain and surface waters can be as high as  $10^6$ . Methyl mercury is mobile within the body because it reacts with the  $-\text{SH}$  ligand in cysteine to form a complex that behaves in the body like methionine and is readily transported across barriers including those for the brain and fetus. Hair, with a growth rate of about 1 cm per month, provides a powerful tool for determining exposure histories in epidemiological studies. Long latent periods, of the order of months, precede the manifestation of effects of mercury exposure. The effects on the central nervous system include the selective inhibition of protein synthesis involving RNA. The most susceptible neurons are those with the least repair capacity. Division and migration of neural cells is inhibited, with the basic target being the microtubules. For practical purposes of safeguarding health, it is useful to define a threshold value. The value that has been used to guide the establishment of guidelines of exposure has been 100 ppm in human hair based on effects observed in adults. Effects on the motor response of babies/children/offspring, however, can be measured at a concentration level in maternal hair of 10 ppm. This poses a tough decision for regulators with about 1% of the population, primarily fish eaters, having levels exceeding this threshold. As was the case for lead, the levels at which effects are being found are alarmingly low.

## Chlorinated Hydrocarbons

The session on chlorinated hydrocarbons, chaired by W. Tsang (National Institute of Standards and Technology) and F. Matsumura (University of California, Davis) contained six presentations. All except that by C. Koshland (University of California, Berkeley) centered on dioxins, their formation, and rates of emission. In her presentation, Koshland described the experimental and theoretical tools that can be applied to determining the chemistry of combustion of chlorinated hydrocarbons and products of incomplete combustion. She reported on studies involving the injection of selected chlorinated hydrocarbons into a turbulent combustion product of a propane air flame followed by monitoring with a fourier transform infrared spectrometer. For temperatures above 1050 K, at which the injected streams ignited, destruction of the compounds was complete. At lower temperatures, a number of by-products, including acetylene, phosgene, and vinyl chloride, were identified. The experimental results were modeled on the basis of elementary single-step processes, and a detailed mechanism was proposed. Kinetic models provided good agreement with the experimental measurement for the disappearance of the injected chlorinated hydrocarbon and the appearance of hydrogen chloride, but did less well in predicting the concentrations of the by-products. Koshland identified the need for improved data on thermodynamic parameters and the elementary rate constants.

There is a large gap in our knowledge on how complex structures such as dioxins can be formed from smaller chlorinated hydrocarbons. The talk by F. Karasek (University of Waterloo) briefly touched on his work on dioxin formation on fly ash, which takes place in a temperature window of 250°C to 350°C. Here, however, the precursors were the chlorinated phenols. He also mentioned work where dioxin formation occurs without the more likely precursors. This is a key issue. The fact that we do not have a definitive picture of how dioxin is formed is an important ingredient in the public perception regarding incineration. Although Karasek suggests that with proper inhibitors, such as CaO and NH<sub>3</sub>, injected upstream of the particulate collection system, dioxin formation can be greatly reduced, but there is still the need to develop an understanding of the detailed chemistry of the behaviors of organics on fly ash. Aside from the short-range benefits, this will lead to the development of a knowledge base of possible additional problems that may arise from hazardous waste incineration. An issue that was addressed is the possibility that other chlorinated organic toxins may be produced during incineration. Soot formation in the presence of chlorine compounds was discussed later in the conference.

The elegant work of R. Hites, (University of Indiana), J. Giesy (Michigan State University), and S. Safe (Texas A&M University) emphasizes how the fate of dioxins in the atmosphere is as important as its formation mechanism in the combustor. This work also demonstrates the power of mode analytical techniques for linking chemicals in remote locations to their sources. Polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/F) are ubiquitous in the environment and are of concern because of the high toxicity of certain congeners. PCDD/F are discharged daily into the environment in low concentrations by industrial and municipal waste incineration, car exhaust, and pulp and paper mill effluents. Once PCDD/F are released into the environment, they become distributed

throughout various environmental compartments, including the atmosphere, which transports PCDD/F long distances. While PCDD/F are transported through the atmosphere, transformations may occur. To address this issue, Hites reported on a detailed, 3-year study of PCDD/F in the ambient air of Bloomington, Indiana. Rainwater was also sampled to investigate the atmospheric deposition of PCDD/F. In addition, the photodegradation of PCDD/F on particulates was examined to study one possible pathway of PCDD/F degradation.

Typical PCDD/F concentrations measured in Bloomington air ranged from 1 to 4 pg/m<sup>3</sup>. All air samples showed a predominance of octachlorodioxin. Total PCDD/F concentrations showed no seasonal variations, but the vapor-to-particulate ratios changed. Vapor-to-particulate ratios varied from 0.01 to 30 and were dependent on the compound's subcooled-liquid vapor pressure and the ambient temperature. Total concentrations of PCDD/F in rain were 10–84 pg/L in the dissolved phase and 37–320 pg/L in the particulate phase. Particulate scavenging is the major wet removal process affecting PCDD/F. Depositional fluxes of PCDD/F were calculated, and dry deposition was determined to be five times more efficient than wet deposition. Photodegradation experiments showed that PCDD/F native to municipal incinerator fly ashes that were black, gray, light gray, and light yellow did not photodegrade after 100 hr of light exposure. Thus, particulate-phase photodegradation of PCDD/F does not appear to be an important removal process.

In summary, the data support the following scenario. A broad range of PCDD/F are introduced into the atmosphere by numerous sources, forming a uniform, urban, ambient air mixture. As the air mass moves away from the sources, it is diluted with cleaner air and starts to "age." Less chlorinated congeners are found to a greater extent in the vapor phase, and thus, they may undergo vapor-phase photodegradation; particulate-phase photodegradation does not occur. This enhances the relative concentrations of the more chlorinated congeners. The particulates, with their enhanced load of the more chlorinated congeners, are deposited by both wet and dry processes. Although the dry process dominates, the efficiency of the wet method improves for the more chlorinated congeners. Once in the water column, Henry's Law constants predict greater vaporization of the less chlorinated congeners. This further enhances the relative proportion of the more chlorinated congeners that pass through the water column to the sediment. All of these processes favor a homologue profile enriched in the more chlorinated congeners. Therefore, octachlorodioxin is most predominant in the sediments. The data suggest that only the most chlorinated PCDD/F congeners are environmentally persistent. This finding may be of interest to policymakers because these congeners tend to be the least toxic.

The effects of chlorinated hydrocarbons on wildlife in the Great Lakes area were described by Giesy. The study was motivated by the persistence of birth defects in the bird populations despite the rapid decrease in the contaminant concentration. Planar chlorinated PCBs and tetrachlorinated dibenzodioxins (TCDD) were suspected. These compounds bind to a cytosolic receptor, cause a transformation of that receptor by loss of a heat shock protein, are translocated to the nucleus where they bind to the DNA, and cause expression changes manifested as enzyme induction. Using toxic equivalency factors (TEF), Giesy determined that in the Great Lakes area that the contribution of

TCDDs relative to PCBs was as little as 1% in industrialized areas to 20% in remote locations. Variation in TCDD/PCB ratio between locations was explained by pharmacokinetics that result in an enrichment of the more toxic compounds. Other compounds of concern are biphenylenes and chlorinated naphthalenes.

It is clear that some dioxins are not readily destroyed in the environment and have drastic effects on wildlife. Thus, even though dioxin is clearly not a short-term health risk, the question of long-term effects certainly warrants close attention. The paper by O. Hutzinger (University of Bayreuth) is notable in pointing out the much stronger regulatory climate in the European community. He traced the fate of dioxins from their formation to ingestion by man. The principal sources were studied including industrial, combustion, and waste sites. Incinerators and scrap reprocessing furnaces were found to be among the major emitters of dioxins. Once in the atmosphere dioxins are transported to plants and through the agricultural food chain to man. Pine needles were noted to have high concentrations of dioxins, PCBs, and DDE and provide a monitoring system as well as a sink for dioxins. A material balance on a cow showed that the major intake was through the fodder and that 20% of the output was in milk. Hutzinger implicated milk products as the main route to man, even though the concentration of dioxins in fish is much higher. In concluding, he noted that regulations introduced in Germany will result in a reduction in the estimated emissions from a current value of 480 toxic equivalents per year to 8 per year in the year 2000. If the Europeans are able to achieve their standards for the dioxins, it would seem that as a practical matter these will in time become the *de facto* standards in the United States. Thus, questions of the validity of dioxins as a priority pollutant will probably be settled on other than a purely scientific basis.

The formation of PCDD/Fs with widely varying congener distribution in organic chemicals and combustion systems provides the motivation for the development of TEFs and was the subject of Safe's presentation. The common biological and toxic responses elicited by different congeners makes hazard assessment of complex mixtures tractable. Different members have the same toxic responses, but different potencies. The evidence for a common receptor-mediated mechanism of action is extensive, including structure-receptor binding relations, structure-induction relations, and structure-toxicity relations. Genetic evidence is critical to developing TEFs. The TEF is defined as the reciprocal of the multiple of the weight of TCDD required to produce the same response. Although the rank order of different responses are the same, as much as 60-fold variation in the TEF may be observed because of differences in pharmacokinetics, metabolism, and binding to receptors and proteins. The values selected are therefore a working compromise. Safe noted that the TEF assigned to octachlorinated dibenzodioxin (OCDD) had been increased from 0 to 0.001. This is of particular significance because OCDD is a major constituent of incinerator emissions. Application of the TEF to the data from the Binghamton office fire was used to show the utility of the concept in providing a composite measure of toxicity.

The present situation on dioxins is similar to that for freons a few years ago. At that time the local impact on skin cancers seemed to be minuscule; however, research continued due to possible long-term effects, and this decision would appear to be fully justified by recent events. Although it has been difficult to isolate

any toxic effects of dioxins in man, the impact on ecological systems seemed to justify the efforts devoted to reduce their emissions.

## Aerosols

The last session, on aerosols, was chaired by D. Chang (University of California, Davis) and R. Frank (Johns Hopkins University) who pointed out the important role that carbonaceous and inorganic aerosols can play both in determining the composition of the gas/aerosol complex present in atmospheres and their health effects.

I. Kennedy's (University of California, Davis) research relates to the formation of soot particles during combustion of chlorinated hydrocarbons. The underlying goal of this study is an understanding of how increased intensity of turbulent mixing can reduce soot formation while simultaneously preventing formation of products of incomplete combustion. He described experiments that have been carried out in a well-defined opposed-flow, laminar, diffusion flame burner. Information regarding effects of turbulent mixing is obtained through knowledge of the strain rates produced by the flow. Mixtures of methane and chloromethane up to equal molar concentrations have been studied under oxidizing conditions to obtain profiles of major and trace organic species, as well as soot particle number and volume concentrations. In addition, species associated with the soot are being identified by extractive sampling. Thus far, chlorinated species associated with the soot have not been observed at measurable levels. Because the flow field is well defined in Kennedy's experimental system, subsequent modeling of chemical kinetics incorporating mixing processes will be possible and is planned in future studies.

T. Novakov (Lawrence-Berkeley Laboratories) illustrated the importance of heterogeneous reaction chemistry in atmospheric transformations of combustion effluents and pointed out the lack of fundamental kinetic data and of an understanding of the important physicochemical phenomena involved. He noted that studies of heterogeneous reaction pathways are few, and it is uncertain what has been overlooked. As a recent example, he cited stratospheric ozone depletion by previously unknown chlorine chemistry on ice nuclei. Novakov further described recent work related to combustion by-products in a cloud chamber (i.e., experiments dealing with the oxidation of sulfur dioxide in the presence of ammonia, water vapor, and various nucleation centers [soot, sodium chloride, and phosphate]). Anomalously fast conversion of the sulfur(IV) to sulfur(VI) in the presence of condensed liquid drops was evident from the data and could not be explained with existing homogeneous liquid phase kinetic mechanisms. The type of nucleation center did not change the conversion rate, but the presence of ammonia was required, and the presence of a condensed phase was found to speed the reaction. Novakov suggested that interfacial phenomena may be playing an important but unknown role in the reaction chemistry of the system.

A. F. Sarofim recounted highlights of a series of collaborative studies, spanning nearly a decade and led by M. Amdur, which brought together combustion engineers, material scientists, and inhalation toxicologists. By burning certain coals in a laminar-flow furnace at 500°C, ZnO, SO<sub>2</sub>, and H<sub>2</sub>O vapor were reacted to form a H<sub>2</sub>SO<sub>4</sub>-coated ultrafine metal oxide aerosol analogous

to those emitted during metal smelting and coal combustion. The toxicological findings were presented by Sarofim in Amdur's absence. Guinea pigs exposed several hours daily for 5 days to the H<sub>2</sub>SO<sub>4</sub>-coated aerosol showed dose-dependent impairment of lung function as well as inflammation and edema of the lung. An approximately 10-fold higher concentration of H<sub>2</sub>SO<sub>4</sub> mist of the same size was required to produce equivalent functional changes. The contribution of the ZnO carrier to the response is under study.

M. Lippmann (New York University) reviewed the epidemiology of acid aerosols, with particular emphasis on the role airborne acids may have played in the pollution episodes that struck London earlier in this century. Considerable effort has been expended reanalyzing and correlating the original limited air monitoring data with the excess mortality and morbidity rates associated with these episodes. Until recently, there have been few direct measurements of airborne acidity made in conjunction with health surveys, so estimates of population exposure have been speculative. Several recently inaugurated surveys are designed to overcome this deficiency.

## Concluding Comments

In the concluding comments, recognition was given to the NIEHS Superfund Basic Research Program and to the major role that Norton Nelson had played in bringing together the different disciplines needed to address environmental problems. The conference illustrated the potential benefits from and the difficulties of fostering interactions between the engineering and health research communities.

## Appendix A

### Health Effects of Combustion By-Products: Program

#### Conference Organizing Committee

Mary Amdur, New York University  
James R. Fouts, National Institute of Environmental Health Sciences  
William Grosshandler, National Science Foundation  
Ronald O. Kagel, Dow Chemical  
Catherine Koshland, University of California, Berkeley  
Fumio Matsumura, University of California, Davis  
Adel F. Sarofim, Massachusetts Institute of Technology  
Martyn T. Smith, University of California, Berkeley  
William A. Suk, National Institute of Environmental Health Sciences

#### Overview

Chairpersons: W. Suk, NIEHS, W. Grosshandler, NSF  
NIEHS basic research related to Superfund  
D. Rall, NIEHS  
Future of incineration: a global perspective  
J. Schofield, Incineration Technology, Inc.  
Defining the appropriate role of incineration  
J. Hirschhorn, EnviroSearch-East  
Review of incinerator design and emissions  
R. Seeker, Energy and Environmental Research Corporation

#### Organic Compounds

Chairpersons: D. Patton, Risk Assessment Forum, EPA, R. Sawyer, University of California, Berkeley  
Flame synthesis of benzene and PAH  
J. Howard, Massachusetts Institute of Technology  
Mechanisms of benzene toxicity: implications for risk assessment  
M. Smith, University of California, Berkeley

#### Formation and persistence of PAH DNA adducts

J. Ross, EPA  
PIC formation from complex waste mixtures  
B. Dellinger, University of Dayton Research Institute  
Analysis of health effects of complex mixtures  
W. Thilly, Massachusetts Institute of Technology  
Discussion: What is a realistic paradigm for assessing the health effects on the plethora of organic combustion by-products?

#### Metals

Chairpersons: J. Fouts, NIEHS, R. Flagan, California Institute of Technology  
Mechanisms of metal emissions  
W. Linak, EPA and J. Wendt, University of Arizona  
Kinetics of elementary combustion reactions of metallic atoms and radicals  
A. Fontijn, Rensselaer Polytechnical Institute  
Mechanisms of nickel carcinogenesis  
M. Costa, New York University  
Role of metallothionein in cadmium toxicity  
C. Klaassen, University of Kansas Medical Center  
Lead and the incineration of municipal solid wastes  
P. Landrigan, Mt. Sinai School of Medicine  
Health effects of mercury  
T. Clarkson, University of Rochester  
Discussion: How does the form of metal emissions influence health impacts?

#### Chlorinated Hydrocarbons

Chairpersons: F. Matsumura, University of California, Davis, W. Tsang, National Institute of Standards and Technology  
Chemistry of chlorinated HC formation  
C. Koshland, University of California, Berkeley  
Health and ecological effects of chlorinated aromatics  
J. Giesy, Michigan State University  
Fly ash catalyzed synthesis and destruction of acid aerosols  
F. Karasek, University of Waterloo, Canada  
The atmospheric fate of combustion-generated dioxins and furans  
R. Hites, University of Indiana  
PCDDs and PCDFs: sources and fates and human exposure  
O. Hutzinger, University of Bayreuth, Germany  
Halogenated aromatic combustion products: hazard risk assessment  
S. Safe, Texas A&M University  
Discussion: Are dioxins from incinerators overrated as priority pollutants?

#### Role of Aerosols

Chairpersons: R. Frank, John Hopkins University, D. Chang, University of California, Davis  
Particulate formation in methyl chloride diffusion flames  
I. Kennedy, University of California, Davis  
Heterogeneous atmospheric reactions of combustion products  
T. Novakov, Lawrence-Berkeley Laboratories  
Role of inorganic aerosols in H<sub>2</sub>SO<sub>4</sub> formation  
A. Sarofim and K. Graham, Massachusetts Institute of Technology  
Health effects of inorganic aerosols/H<sub>2</sub>SO<sub>4</sub>  
M. Amdur, New York University  
Epidemiology of acid aerosols  
M. Lippmann, New York University

#### Closing Remarks

A. Sarofim, Massachusetts Institute of Technology  
D. Hoel, NIEHS

## Appendix B

### References for Further Reading

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